



DOE Photovoltaics Subprogram

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Si:H Materials and Solar Cells Research at Penn State

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Progress in Research on Si:H

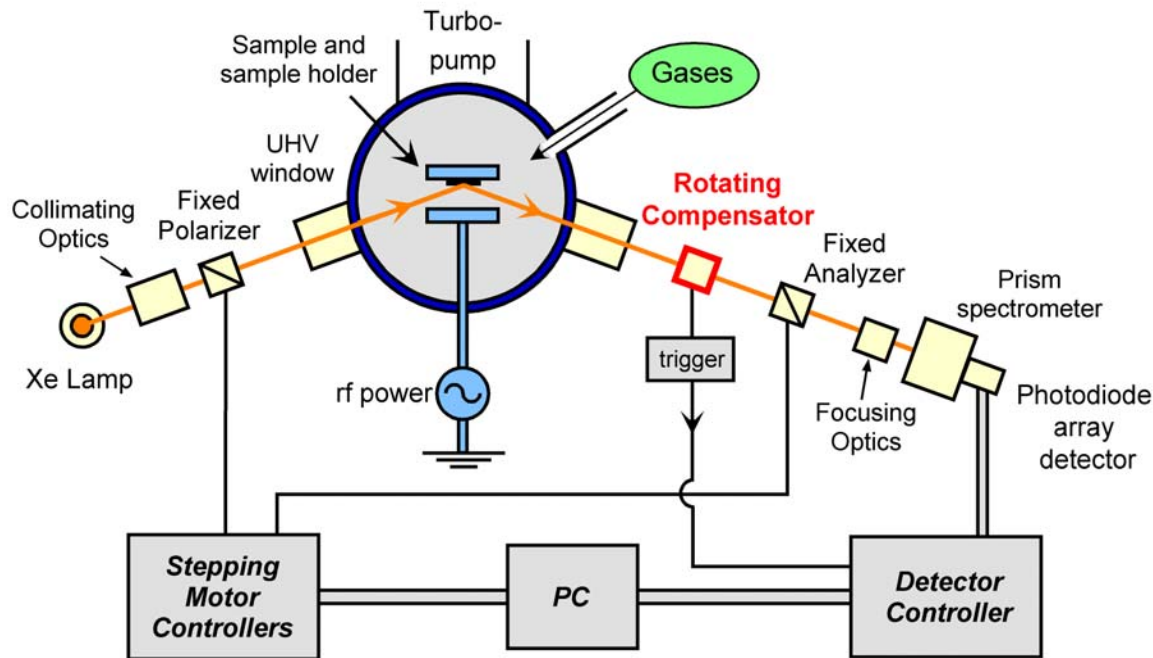
Materials and Solar Cells

A **comprehensive** understanding is being developed of Si:H material growth, microstructure, properties; mechanisms limiting p-i-n, n-i-p solar cell performance and stability.

- Developed *Real-Time Spectroscopic Ellipsometry* for *in-situ* characterization of growth and evolution of microstructure in both films and solar cells. (Now being applied by others)
- Developed *new approaches* for characterizing carrier recombination and the multiple defect states in a-Si:H films and solar cells. (Past focus on just one defect state D^0)
- Developed *deposition phase diagrams* identifying the *microstructural transitions* during growth from amorphous to mixed phase to a single microcrystalline phase. (Powerful guide in material optimization)



- Identified “*protocrystalline*” a-Si:H from its growth and microstructural evolution with thickness and substrate dependence. (Novel concept of a-Si:H deposited with hydrogen dilution representing the growth of such materials with outstanding properties)
- Applied concept of *protocrystallinity* in optimizing intrinsic and doped materials as well as solar cell structures. (Systematic approach)
- Identified, separated and quantified carrier recombination in both p/i regions and bulk intrinsic layers of solar cells. (Not carried out in past)
- Characterized carrier recombination in amorphous and mixed phase (a+ μ c) materials with their effect on solar cell characteristics. (Importance not recognized in past)
- Obtained the “*elusive*” direct correlations between light induced changes in a-Si:H films and corresponding solar cells. (Not established in past)
- Addressed issues regarding nature, origins of different light induced defects in a-Si:H and their dependence on microstructure. (Despite extensive studies in past generally ignored)



- Developed at PSU – recently being applied in other laboratories
- Allows in situ characterization of growth (surface roughness) microstructure, optical properties 1.5 to 4.5eV
- Acquisition time ~50ms allows monolayer growth to be characterized

Suitable for analysis of inhomogeneous films with micro/macro/geometric scale structure



Evolution of Surface Roughness during Si:H Film Growth at Various R on R=0 Substrate

Dilution ratio in PECVD $R=[H_2]/[SiH_4]$

H_2 dilution **extensively** used in fabrication of Si:H materials and solar cells

Two microstructural/phase transitions vs. thickness:

Roughening Transition

$a \rightarrow (a+\mu c)$ mixed phase

$d_b = 3000 \text{ \AA}$ for $R=15$

$d_b = 700 \text{ \AA}$ for $R=20$

$d_b = 200 \text{ \AA}$ for $R=40$

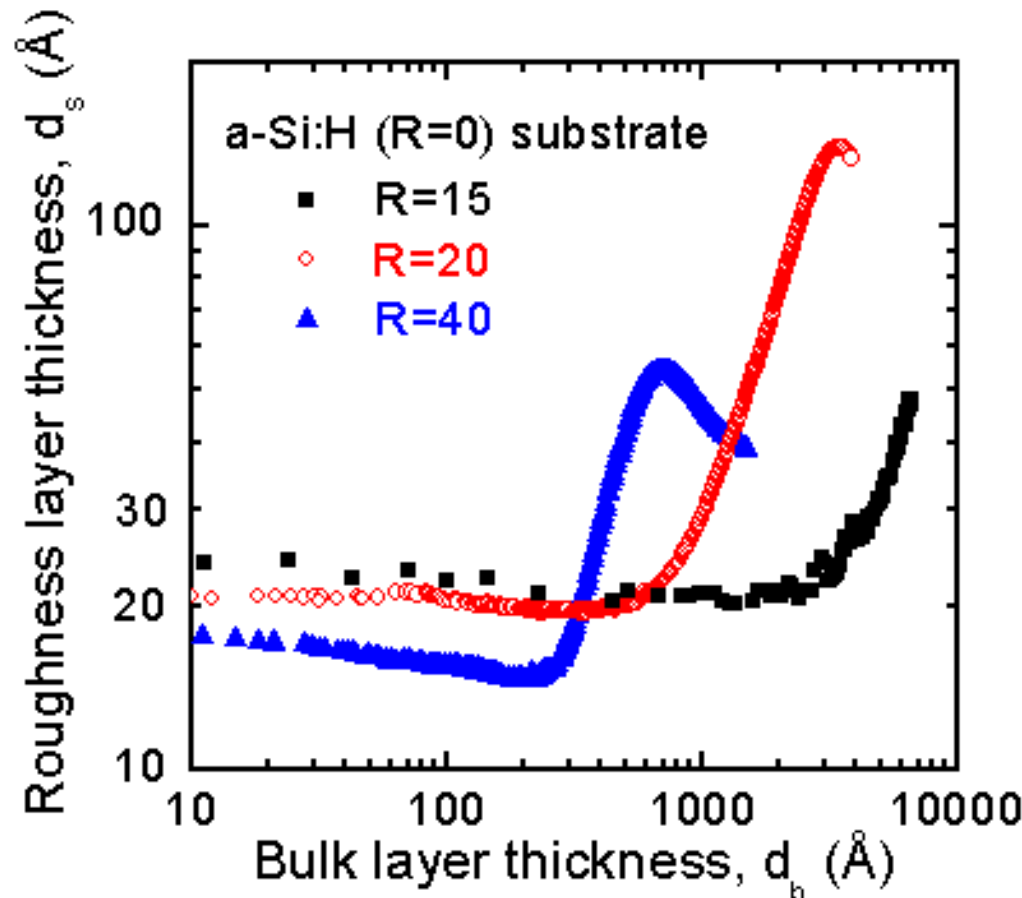
Smoothing Transition

$(a+\mu c)$ mixed phase $\rightarrow \mu c$:

$d_b > 7000 \text{ \AA}$ for $R=15$

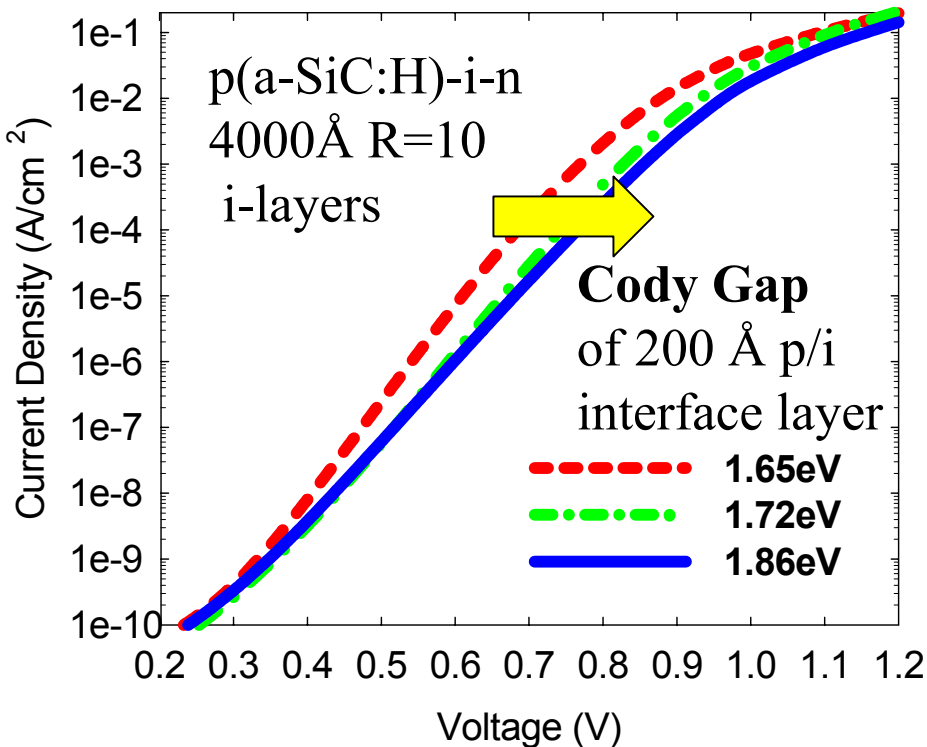
$d_b = 3500 \text{ \AA}$ for $R=20$

$d_b = 650 \text{ \AA}$ for $R=40$



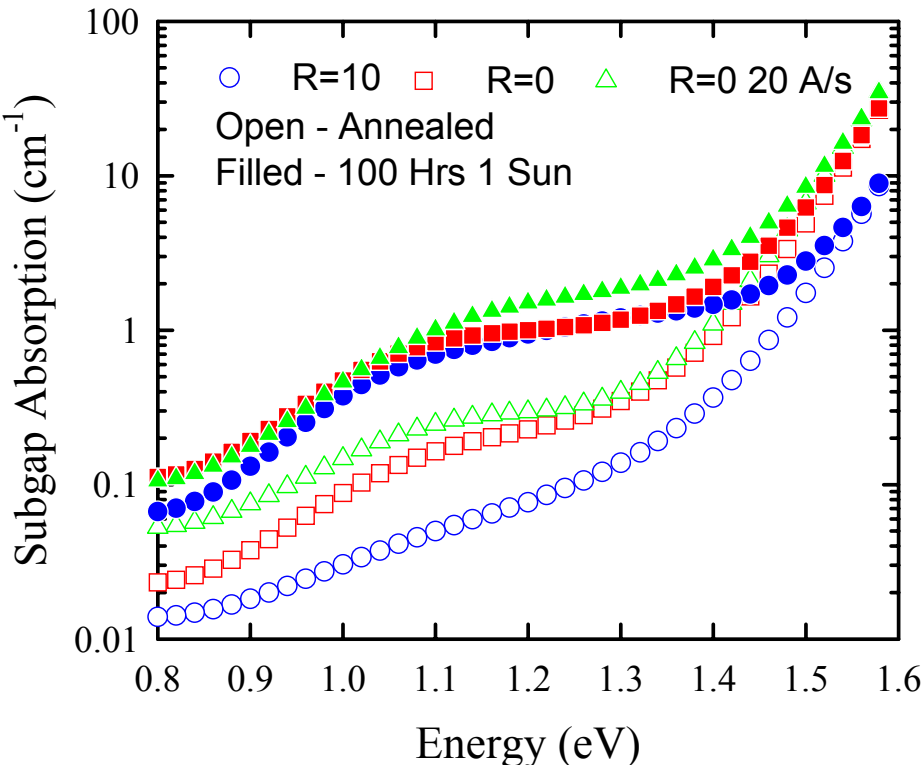


Characterization of Recombination in Solar Cells From Dark Current-Voltage Characteristics



Information about the gap states in the intrinsic layers can be obtained directly from the bulk recombination.

- Clear separation of p/i interface recombination from that in the bulk of a-Si:H solar cells has not allowed J_D -V to be used in characterizing gap states.
- Bulk recombination has been identified and quantified by systematic reduction of p/i contributions in cell structures
- Cell structures are studied in which the two components of carrier recombination are clearly separated.



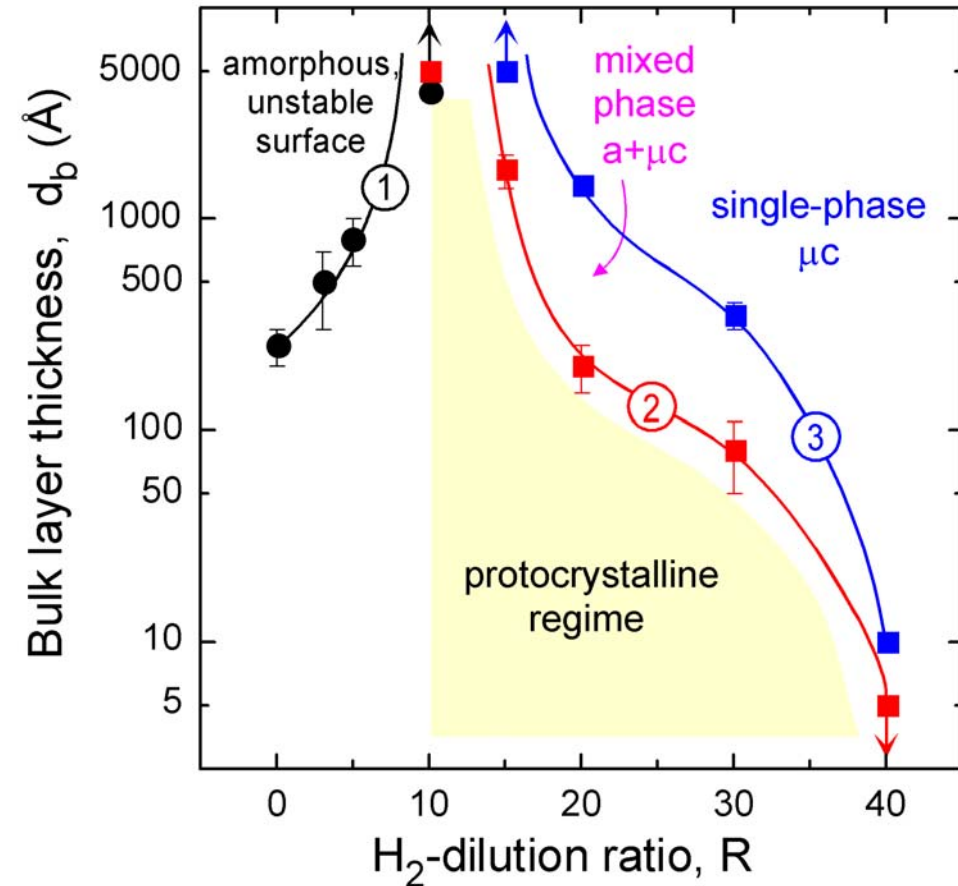
In characterizing recombination in a-Si:H important to take into account presence of multiple defect states.

- **Magnitude** of subgap absorption $\alpha(E)$ extensively used to measure defect states densities
- Interpreted in term of a **single defect**
- **Recombination from multiple defect states** can be identified from dependence of $\mu\tau$ on G
- Differences in **shape** of $\alpha(E)$ point to the contributions of multiple defect states $N(E)$
- $\alpha(E)$ spectra can be related to the distribution of these states by taking the derivatives

$$kN(E) = (\hbar\nu) d[\alpha(\hbar\nu)]/dE - \alpha(\hbar\nu)$$
- (Pearce, et al., *3rd World PV Energy Conv. Conf.*, 2003)



Extended Phase Diagram: Si:H Growth on c-Si/oxide Substrates



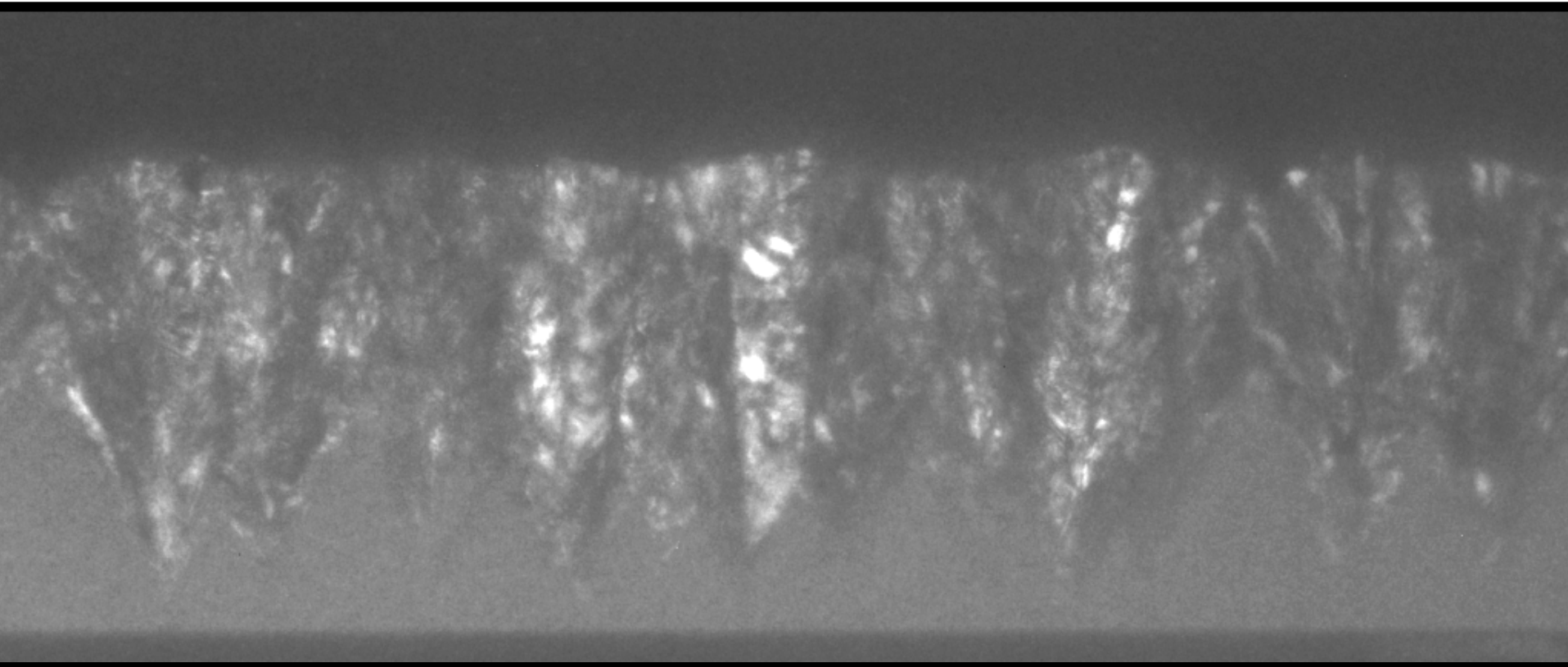
Obtained from the three transitions detected during Si:H film growth:

- (1) $a \rightarrow a$
surface roughening transition
- (2) $a \rightarrow (a+\mu c)$
surface roughening transition
- (3) $(a+\mu c) \rightarrow \mu c$
surface smoothing transition

These transitions provide insights into materials and device optimization

Narrow window for protocrystalline Si:H growth in a thick layer is centered at $R=10$; here the film surface is stable throughout deposition.

Microstructure and its evolution is strongly dependent on substrate

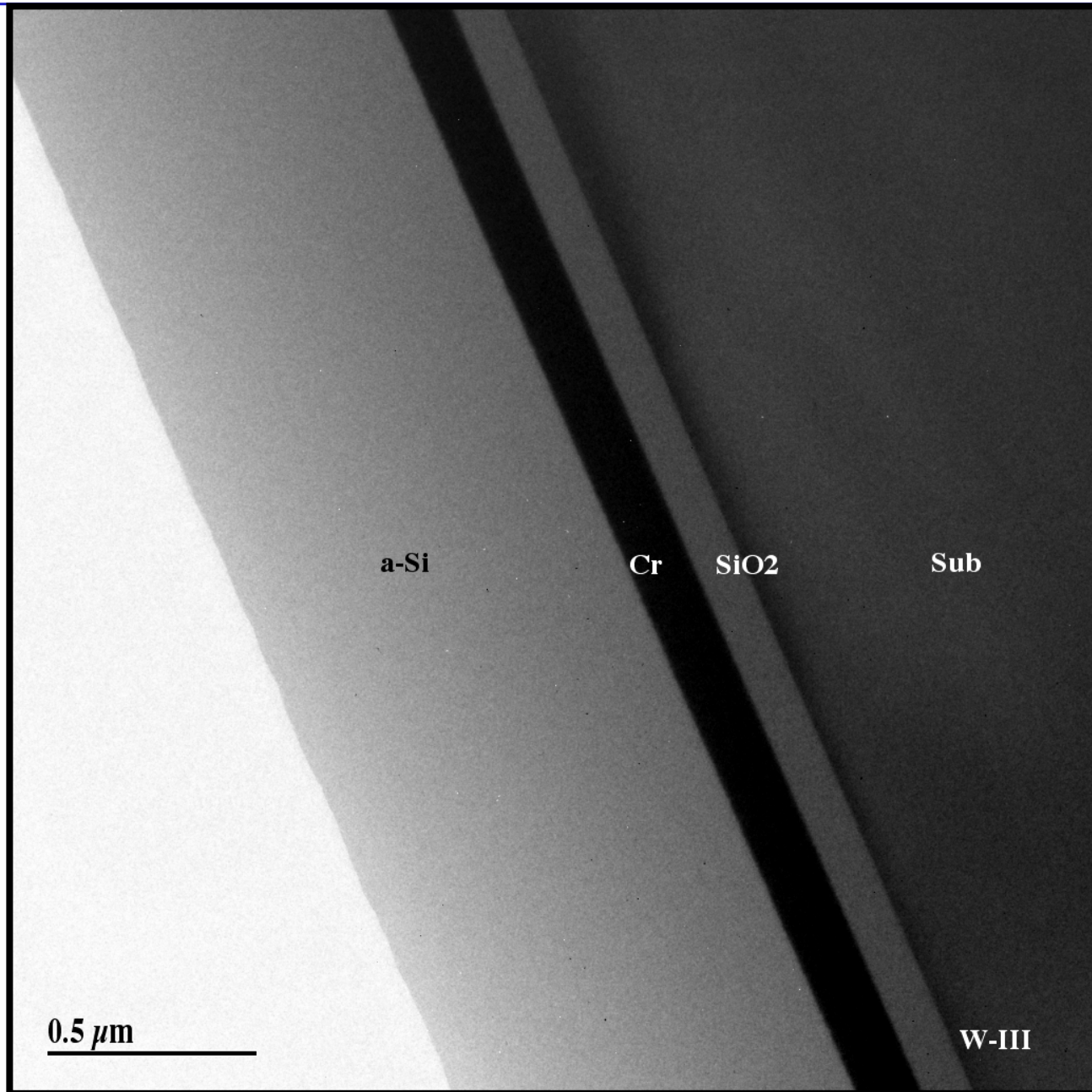


200 nm



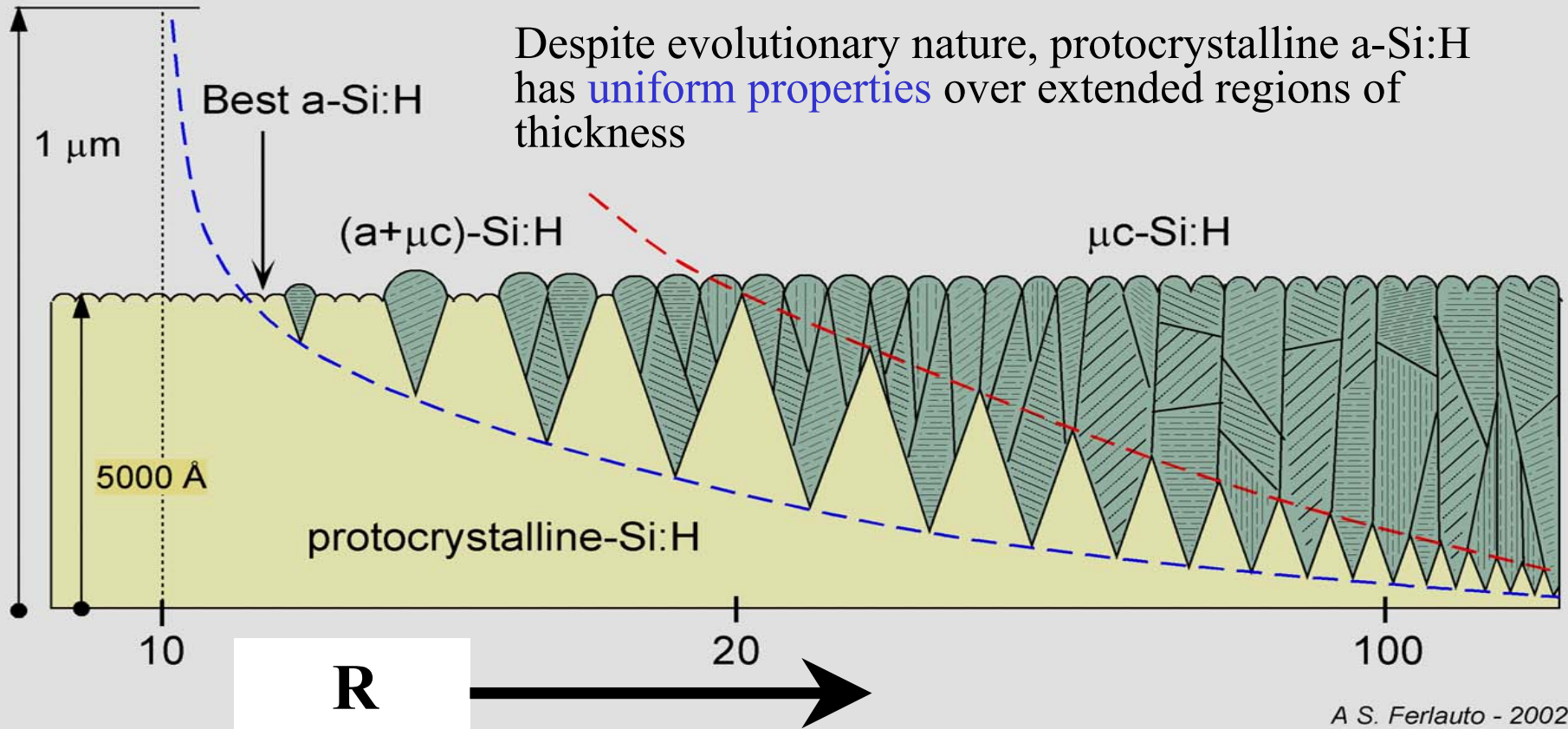


TEM of Si:H deposited with R=10 on Cr (evap)

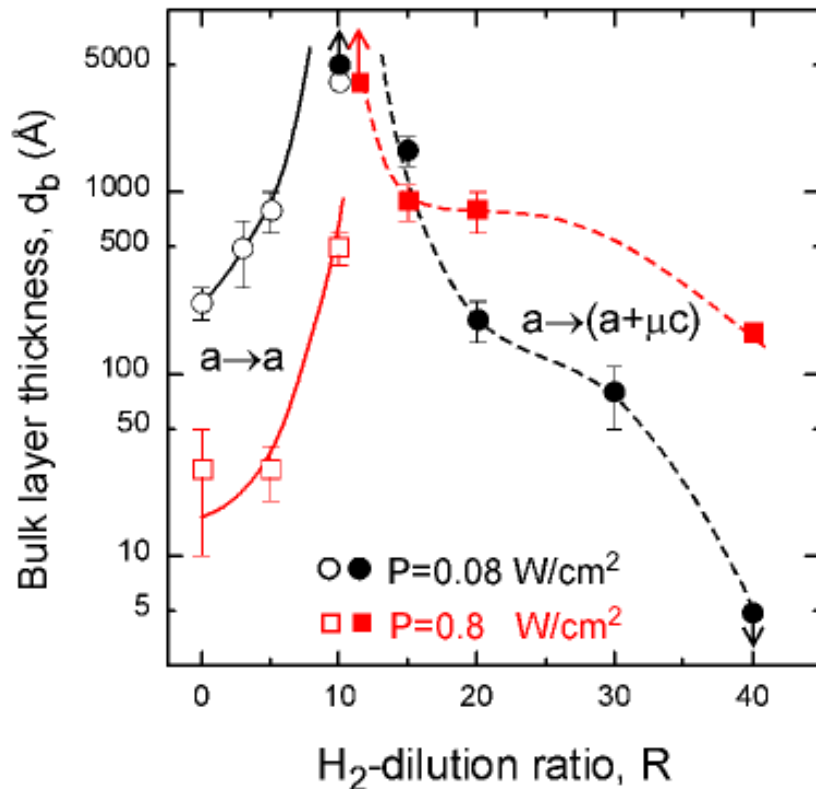




Schematic of the structure of Si:H films on a-Si:H (R=0)



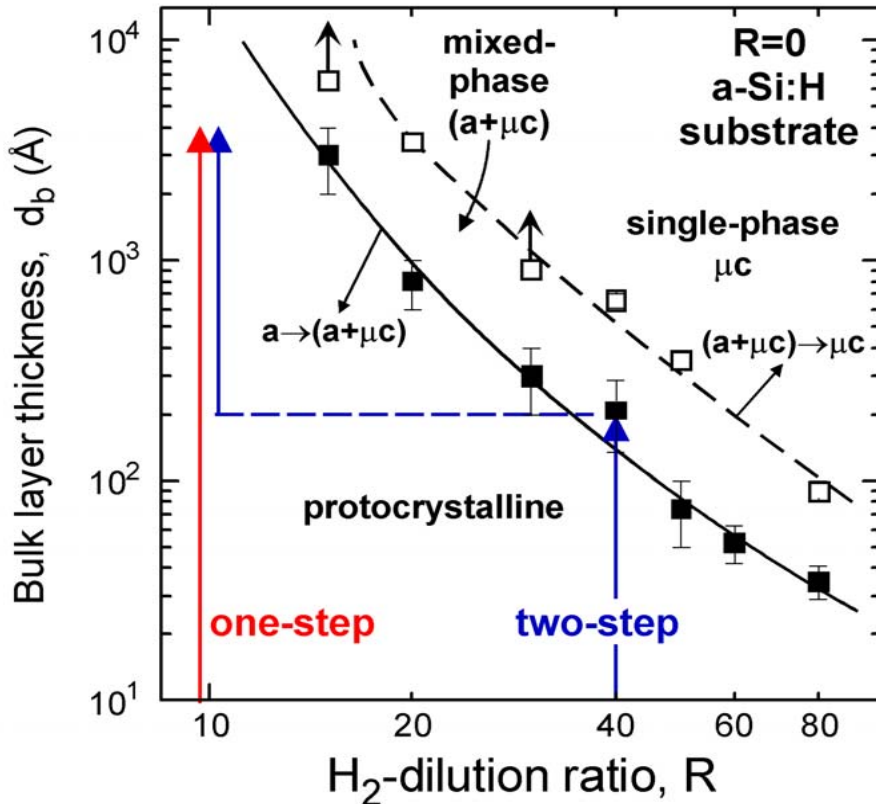
- Great attention must be given to the transition $a \rightarrow (a+\mu c)$ and its **thickness dependence on R**- films and cells
- Phase diagrams are a **powerful guide** in optimizing deposition conditions for fast growth



- Phase diagrams depend on deposition conditions other than R .
- Identify effect of deposition parameters on $a \rightarrow a$ and $a \rightarrow (a + \mu c)$ transitions; regimes of protocrystalline Si:H growth.
- Large shifts in transitions when the plasma power is increased.

Phase diagrams are a powerful guide in optimizing deposition conditions for fast growth.

Optimization Principle for Two-Step i-Layer of a-Si:H p-i-n Solar Cell



Two step optimization of R=10 bulk i-layers with R=40 p/i 200Å layer

Improvement:

- Voc 0.86 to 0.92V
- Annealed FF same 0.72
- DSS FF 0.60 to 0.66

Optimization principle

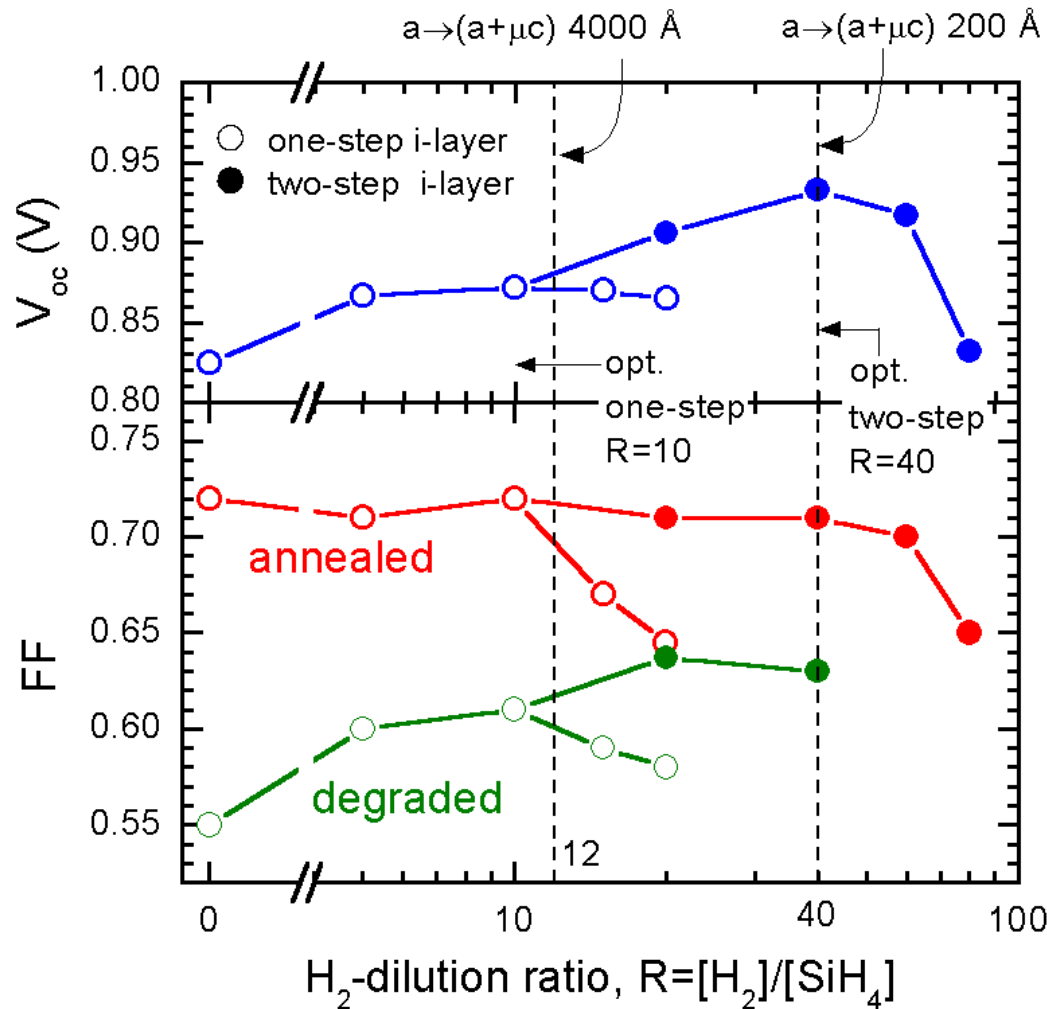
- Prepare interface and bulk i-layers with the maximum $R=[H_2]/[SiH_4]$ values possible without crossing the $a \rightarrow (a+\mu c)$ transition for the desired thickness \Rightarrow **concept of protocrystallinity is useful**

Difficulties

- If the $a \rightarrow (a+\mu c)$ transition is crossed accidentally in this process, one must decrease R below 10 (below protocrystalline regime) to suppress continued growth of the microcrystallites \Rightarrow **real time monitoring and control are needed**



Performance of p(a-SiC:H)-i-n Solar Cells with One-Step and Two-Step i-Layers



Summary of a detailed study based on phase diagrams on the optimization of cell performance

Improvement:

V_{oc} 0.86 to 0.92

Annealed FF same 0.72

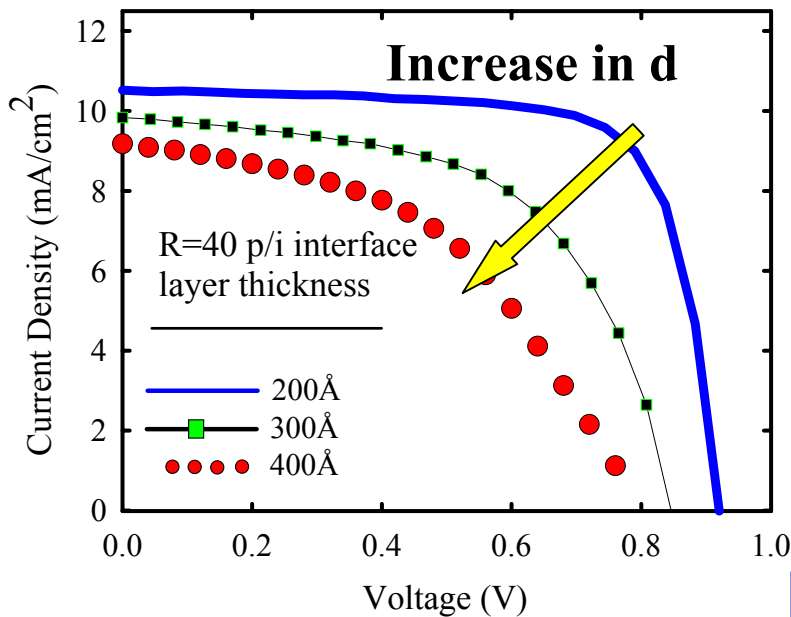
DSS FF 0.60 to 0.66

Note: Optimum performance with $R=40$ adjacent to p-a-SiC:H limited to 200Å thickness.



Nature of (a+ μ c) phase and its effect on solar cell performance

4000Å p(a-SiC:H)-i-n
R=10 i-layer



- From RTSE and AFM for R=40 on R=0 film onset of μ c nucleation occurs at thickness of 200Å, with complete coalescence of μ c nuclei within d=400Å.
- Increase in recombination due to reduction in the mobility gaps in R=40 layer to 1.62eV at 300Å and 1.22eV at 400Å.
- **Presence of such an a \rightarrow (a+ μ c) transition greatly increases carrier recombination and has profound effect on cell characteristics.**

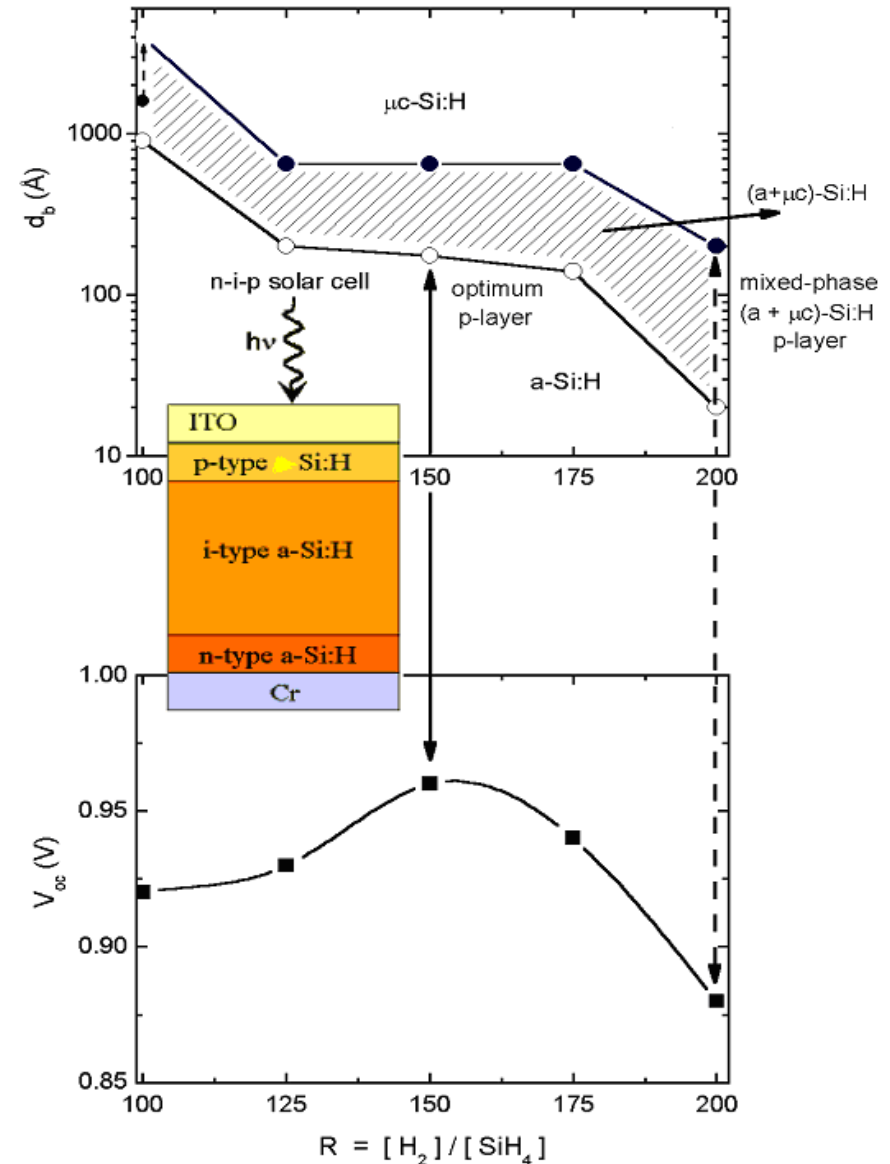
Such phase transitions are even more critical in n-i-p structures where the (a+ μ c) phase is in direct contact with the p-layer.



Protocrystallinity Concept applied to *p-Si:H* Contacts in n-i-p Cells

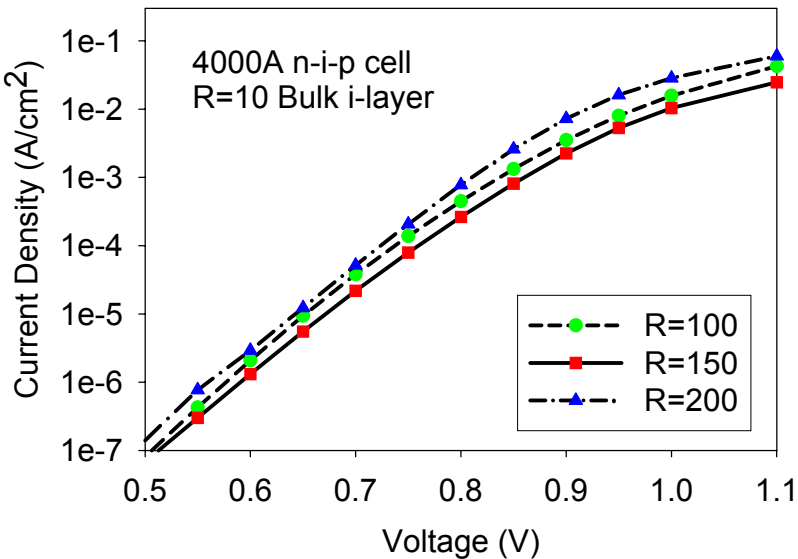
- Phase diagrams of *p-Si:H* layers on $R=10$ *a-Si:H* were used in optimizing V_{OC} in n-i-p cells.
- The maximum V_{OC} occurs with $R=150$ and corresponds to a **protocrystalline layer** terminated at 200\AA or close to the $(a+\mu c)$ phase.
- The lowest V_{OC} is obtained with $R=200$ where the layer has evolved into a purely μc -*Si:H* phase – because i/p recombination increases significantly.

The **erroneous** conclusions that highest V_{OC} 's are obtained with μc *p-Si:H* held for a long time is due to characterizing microstructure on layers $\gg 200\text{\AA}$.





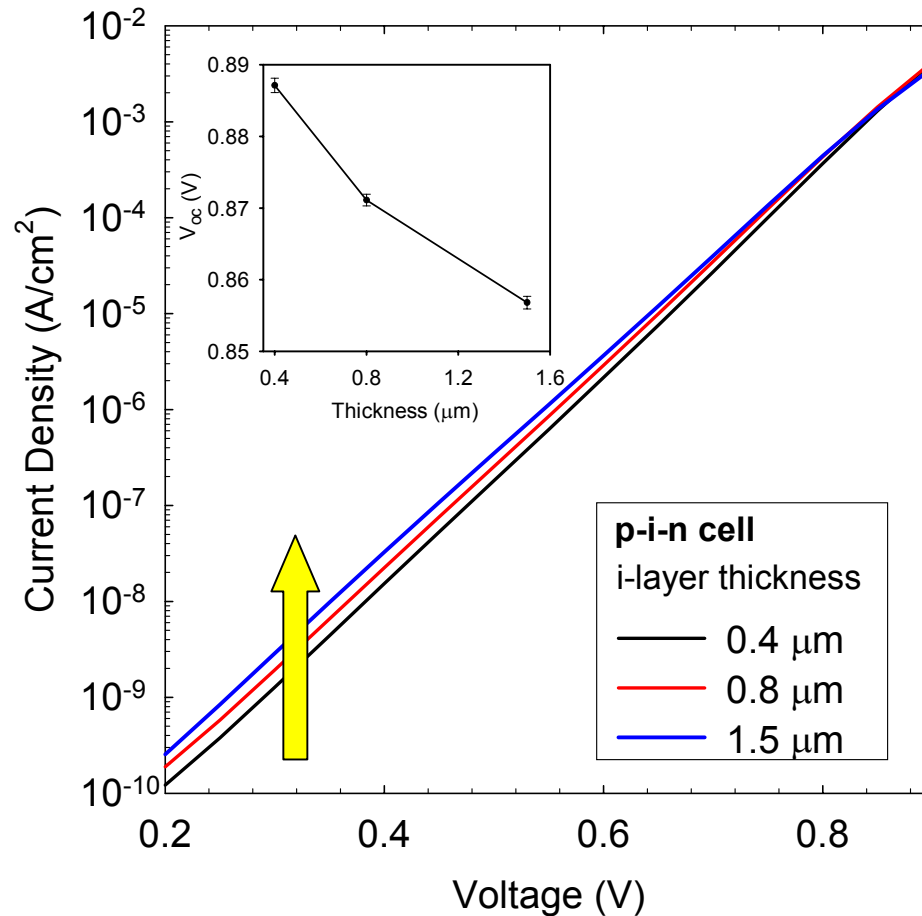
Limitations on 1 Sun V_{oc} imposed by p/i Interface Recombination



- Systematic increases in 1 sun V_{oc} found with decrease in p/i interface recombination for protocrystalline Si:H and a-SiC:H p-contacts.
- Very large increase in such recombination in n-i-p cells with p-Si:H occur when (a+ μ c) phase at or near i-layer ($R=200$).
- The p/i recombination for the $R=150$ p-Si:H is significantly lower than the lowest achieved with a-SiC:H two step processes

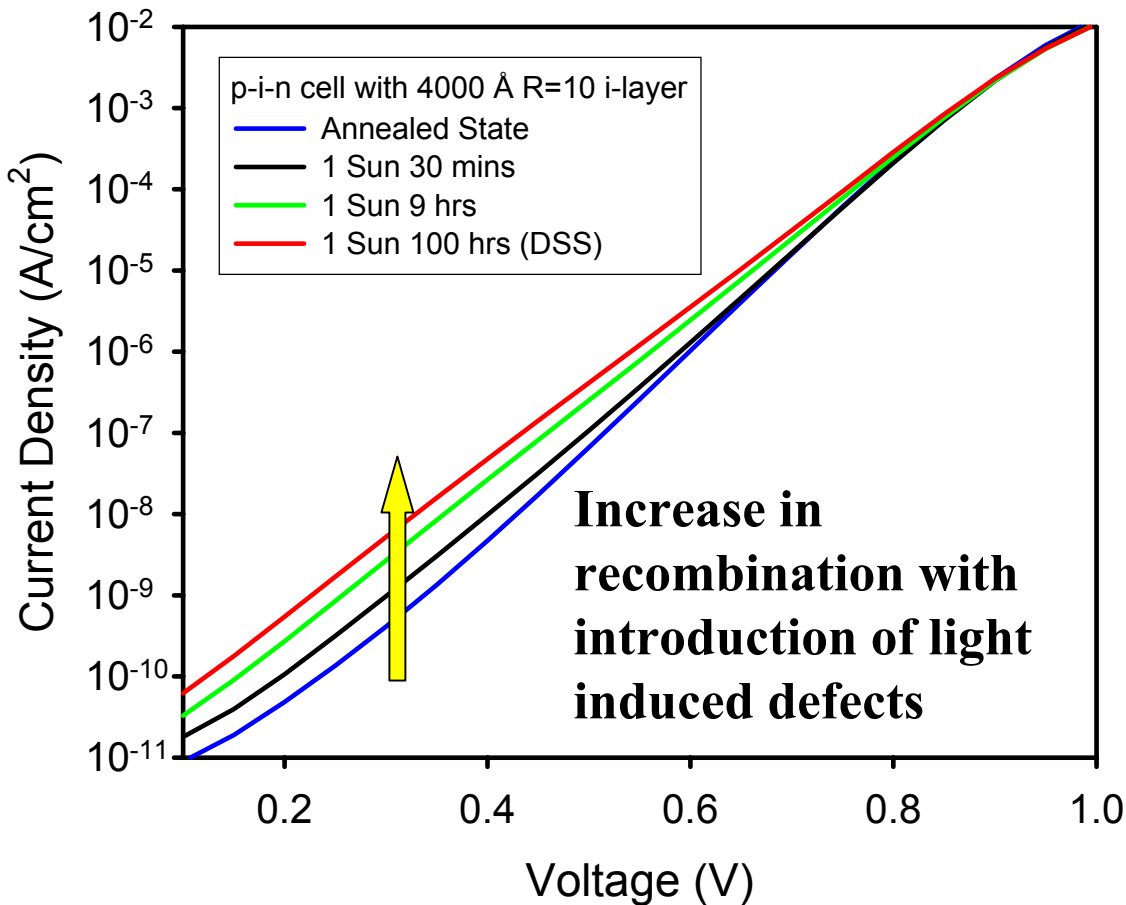
This explains why the highest values of V_{oc} are with p-a-Si:H cells

Defect states in the intrinsic layers of a-Si:H solar cells with low p/i interface recombination



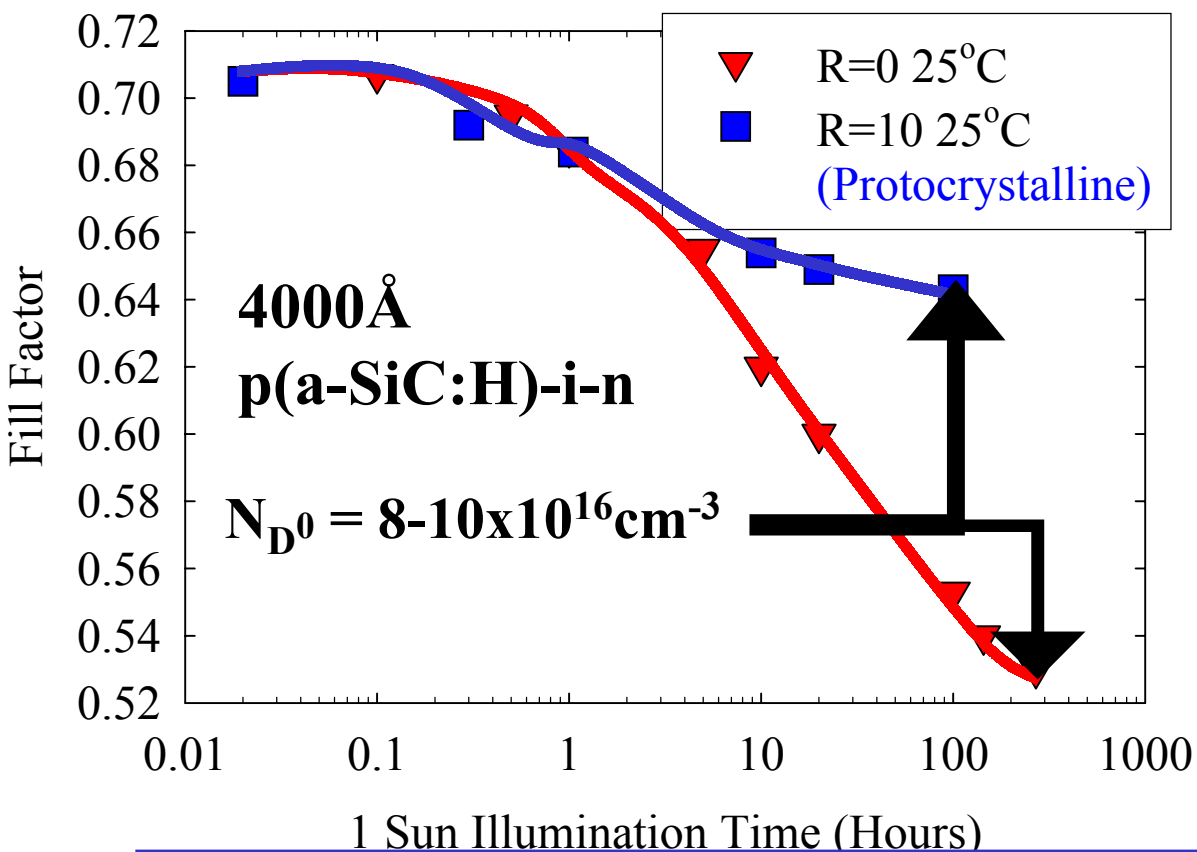
The ability to characterize bulk recombination enables its limitations on different solar cell parameters to be quantified (e.g. V_{OC}).

- Non-uniform distributions of defect states across solar cells predicted by the Defect Pool Model have often been reported.
- No evidence is found from J_D -V characteristics whose bulk contributions are clearly identified.
- Dependence on i-layer thickness, equivalence of p-i-n and n-i-p structures.
- Recombination consistent with spatially uniform defect states and those in corresponding films.



- The kinetics of the light induced changes in J_D -V characteristics are similar to those in FF of cells and the $\mu\tau$ products in corresponding films.

J_D -V characteristics offer an new probe for investigating the nature and densities of defect states in intrinsic layers of solar cells.

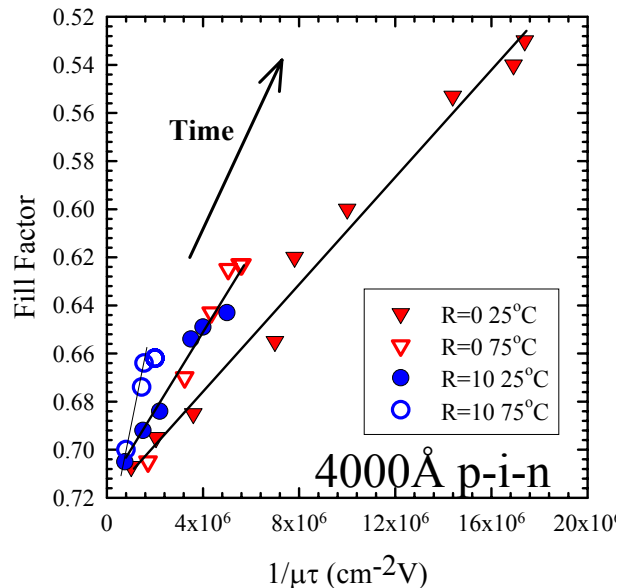
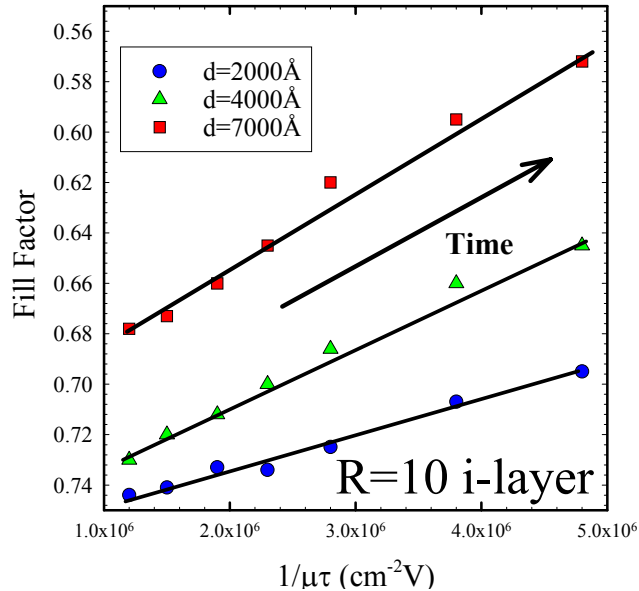


- Extensively used in characterizing light induced defects in solar cells.
- Find kinetics in cells having i-layers with different microstructure clearly point to creation of **multiple defects**.

Multiple defects confirmed with the lack of correlation in the FF degradation with N_{D0} (as measured with ESR), $|\alpha(E)|$, and presence of “fast” and “slow” states.

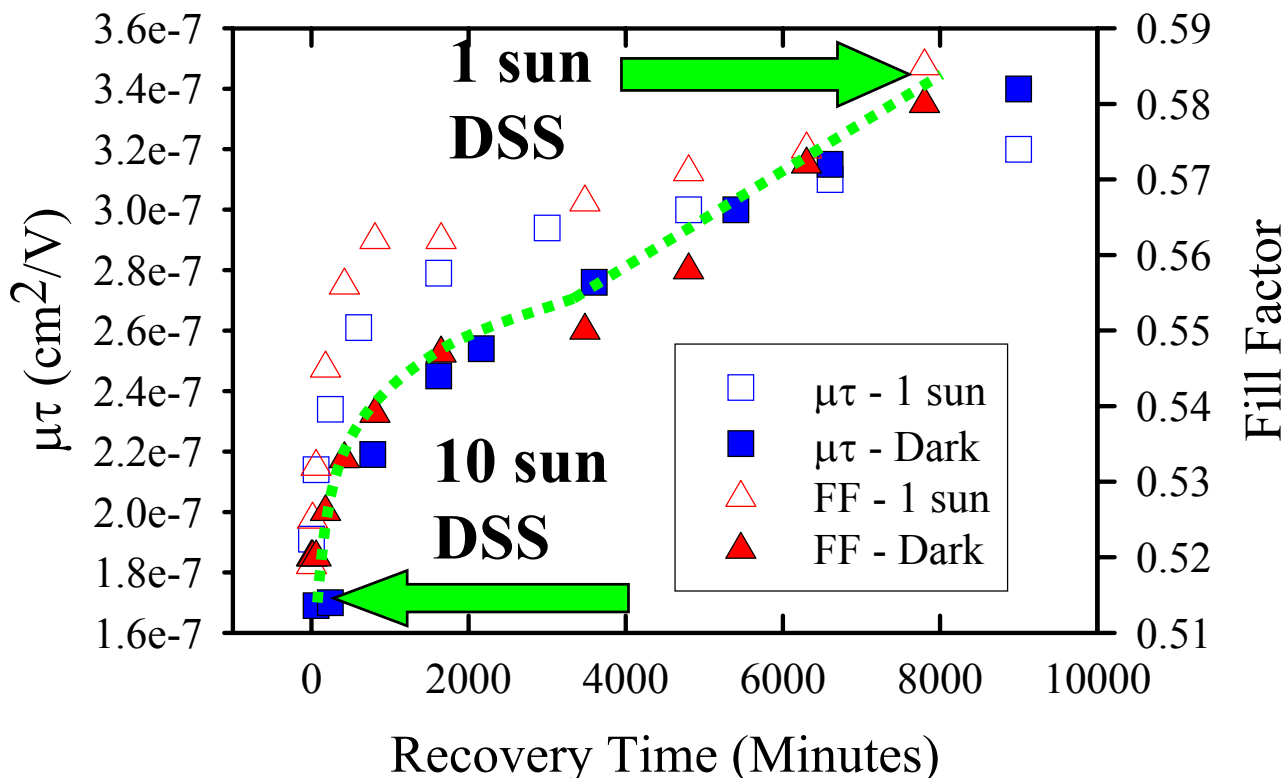


Direct correlation of recombination in films and cells



- The “*elusive*” correlations between light induced changes in thin films and those in solar cells have been established.
- Because the nature and densities of the different defect states in films and cell i-layers are *not yet known* it is not possible to directly correlate them.
- Can *however* relate them through their role as *carrier recombination centers*, N_r where $\mu\tau \propto 1/N_r$, $(1-FF) \propto N_r$

Linear relationships are obtained between $1/\mu\tau$ and FF for cells having different thickness, different i-layers and at different temperatures.



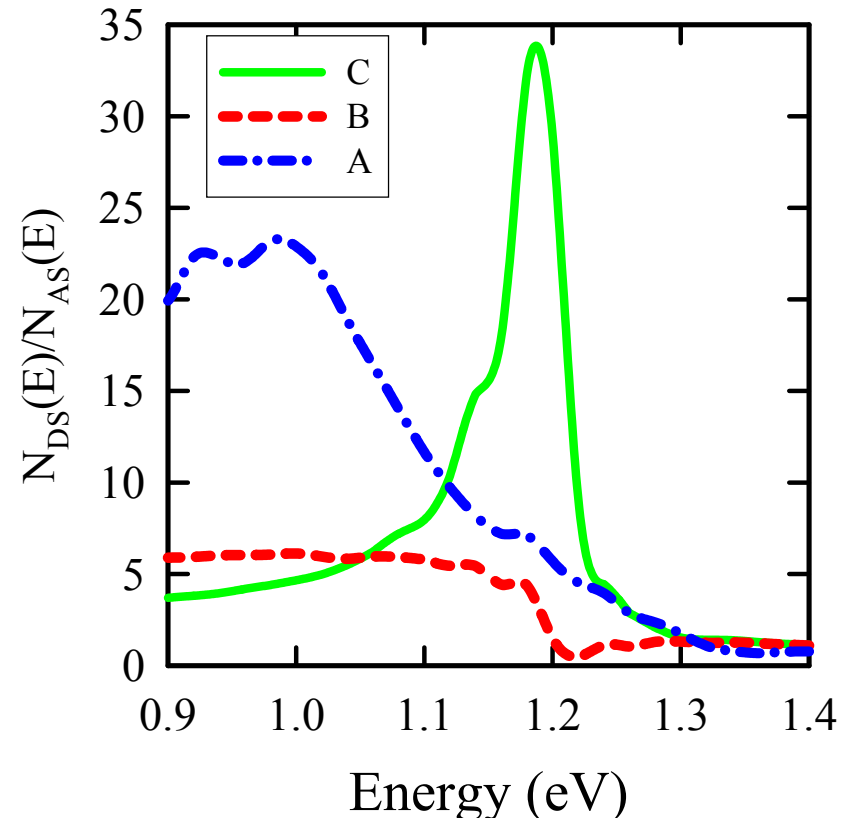
- Same annealing kinetics found for FF and $\mu\tau$ after degradation with high intensity of illumination (Dark and under 1 sun)
- Established presence of “fast” and “slow” in thin films previously only observed directly in solar cells.

Correlation of FF and $\mu\tau$ not only in creation but also in annealing out of defect states.



Distinctly different light induced defect states at and below midgap in a-Si:H

- Evolution of $kN(E)$ from $d[\alpha(h\nu)]/dE$ in degraded state (DS) **normalized** to annealed state (AS)
- **Distinctly different** states created around **1.0** and **1.2eV** from E_C
- Improved microstructure
(**C** $R=0$ **20Å/s** to **B** $R=0$ **1.5Å/s** to **A** $R=10$)
 - Systematic suppression of 1.2eV defects

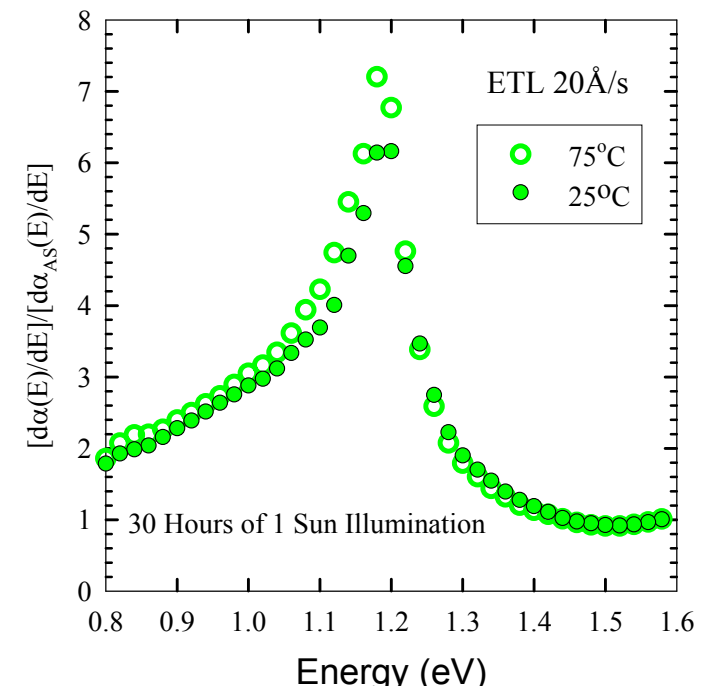
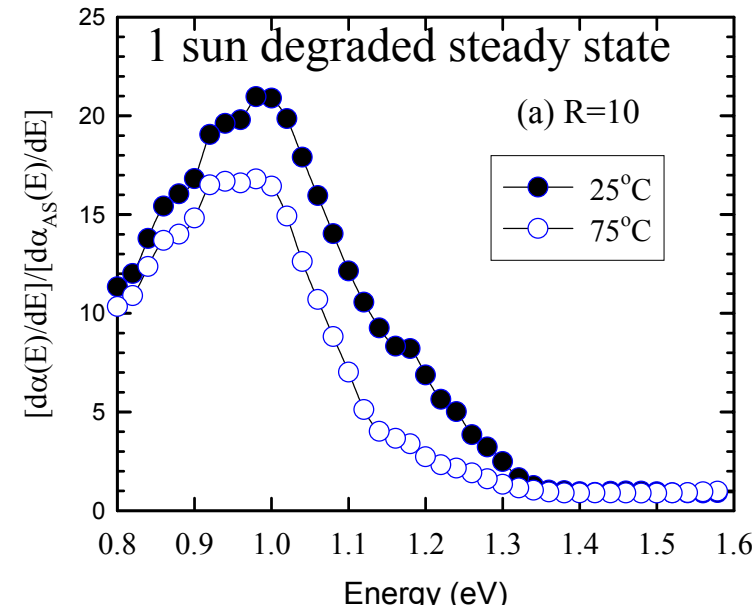


- Evolutions of defects and their temperature dependence self-consistent with changes in FF and $\mu\tau$
- Only in protocrystalline a-Si:H is the defect state at 1.0eV dominant



- Degraded States after 1 sun illumination at 25, 75°C kN(E) Spectra Normalized to AS
- In **R=10**, suppression of defects at 75°C, particularly at 1.2eV, consistent with corresponding higher FF, $\mu\tau$
- No change in spectrum of **R=0 20Å/s** consistent with virtually the same $\mu\tau$ degradation kinetics at both temperatures.

Presence of multiple defect states and their dependence on microstructure must be taken into account in characterizing stability of solar cell materials and SWE.





- RTSE is a *unique and powerful* technique for development of phase diagrams.
- Deposition phase diagrams *extremely useful* in optimization of Si:H materials for solar cells.
- Concept of *protocrystallinity* shown to be useful in:
 - *Improvement* of n, i, and p Si:H layers
 - *Systematic* improvement of cell structures
 - *Controlling* deleterious effects of a \rightarrow (a+ μ c) transition on solar cell characteristics
 - Overcoming *erroneous* conclusions drawn from characterizing films thicker than the layers used in solar cells.



- **New approach for characterizing $\alpha(h\nu)$ spectra has:**
 - Offered a *more reliable* method for evaluating materials for solar cells.
 - Identified evolution of *distinctly different* light induced defects.
 - Points to a reason for the *discrepancies* between stabilities claimed for *films* and those found in corresponding *solar cells*.



- Identifying p/i recombination in solar cells *key* to characterizing i-layers and their contributions to cell characteristics.
- J_D -V characteristics used as a *new probe* for characterizing recombination and defect states in intrinsic layers of solar cells.
- Presence of *spatially uniform densities* of defects in the i-layers in conflict with Defect Pool Model but allows correlations with corresponding films.
- “*Elusive*” direct correlations between recombination in thin films and their solar cells established.
- *Same* creation and annealing kinetics of “fast” and “slow” states established for FF and $\mu\tau$.
- For the *first time* distinctly different light induced defect states centered around 1.0 and 1.2 eV have been clearly identified.



- The results on the two distinctly different light induced defect states in a-Si:H are significant in that:
 - They are *consistent* with the discrepancies between changes in dangling bond densities, N_D^0 , and those in FF, $\mu\tau$.
 - Their evolution is *consistent* with that of “fast” and “slow” states.
 - They are *consistent* with changes in stability of a-Si:H with different microstructure.
 - They show improved stability of *protocrystalline* a-Si:H is accompanied by *suppression of the 1.2 eV defect state*.
 - They *point out* the serious limitations of the commonly used methodologies of assessing the stability of solar cell materials.
- The established presence and distinctly different evolutions of the two light induced states *are not consistent* with a variety of explanations proposed for the origin of the Staebler-Wronski effect.



Absence of carrier recombination associated with the defect pool model in intrinsic amorphous silicon layers: Evidence from current-voltage characteristics on $p-i-n$ and $n-i-p$ solar cells

Society

... and 10 Invited Talks at International Conferences and Workshops

2002

presented and differing in de which illustrate of two distinctly below midgap

***p*-type layers**

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(Received 11 April

In studies of hy plasma-enhanced circuit voltage (V in nature. Specifically using the maximum transition into the p -layer thickness i -layer phase als American Institu

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We have developed a Kramers-Kronig consistent analytical expression to fit the measured optical functions of hydrogenated amorphous silicon (a -Si:H) based alloys, i.e., the real and imaginary parts of the dielectric function (ϵ_1, ϵ_2) (or the index of refraction n and absorption coefficient α) versus photon energy E for the alloys. The alloys of interest include amorphous silicon-germanium (a -Si_{1-x}Ge_x:H) and silicon-carbon (a -Si_{1-x}C_x:H), with band gaps ranging continuously from ~ 1.30 to 1.95 eV. The analytical expression incorporates the minimum number of physically meaningful, E independent parameters required to fit (ϵ_1, ϵ_2) versus E . The fit is performed simultaneously throughout the following three regions: (i) the below-band gap (or Urbach tail) region where α increases exponentially with E , (ii) the near-band gap region where transitions are assumed to occur between parabolic bands with constant dipole matrix element, and (iii) the above-band gap region where (ϵ_1, ϵ_2) can be simulated assuming a single Lorentz oscillator. The expression developed here provides an improved description of ϵ_2 (or α) in the below-band gap and

Realtime spectra applied to develop de the thickness evolution (Si:H) thin films establish optimization incorporated into hig amorphous Si:H (a -i growth of Si:H on a transitions versus acc amorphous to the crystalline) growth n the second from the crystalline growth r